Project ID: **BAT402**

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IMPROVING BATTERY PERFORMANCE THROUGH STRUCTURE-MORPHOLOGY OPTIMIZATION

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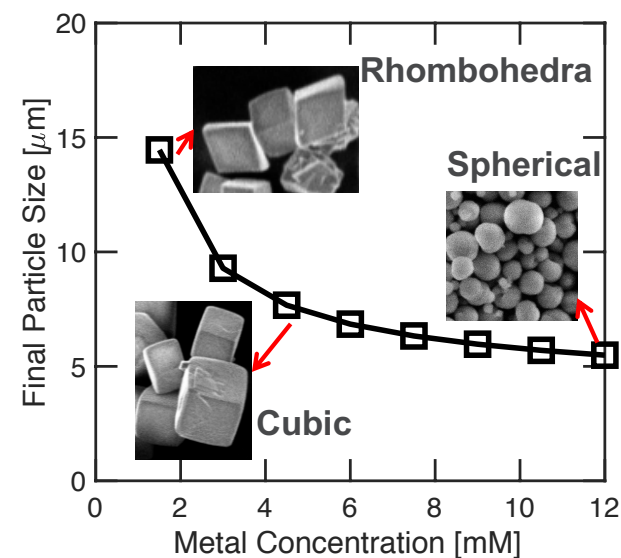
UChicago ▸
Argonne LLC

U.S. DEPARTMENT OF ENERGY

OVERVIEW

Timeline

- Start date: October 2018
- End date: September 2021
- Percent complete: 55%

Barriers

- Limited control on particle structure/morphology during synthesis of NMC cathodes
- High cost of sintering and calcination
- Low density and conductivity during sintering of solid electrolytes

Budget

- $450k/year
  - 1.5 FTE Scientist
  - 1.0 FTE Postdoc

Partners

- Greg Krumdick and Joseph Libera (MERF, ANL), Project ID: BAT315
- Ozge Kahvecioglu and Shankar Aryal (MERF, ANL), Project ID: BAT167
- Jason Croy and Arturo Gutierrez (CSE, ANL), Project ID: BAT049
- Feng Wang (BNL), Project ID: BAT183
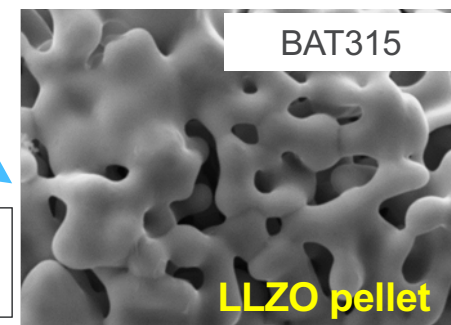- Joanne Stubbs and Peter Eng. (U. Chicago, APS)
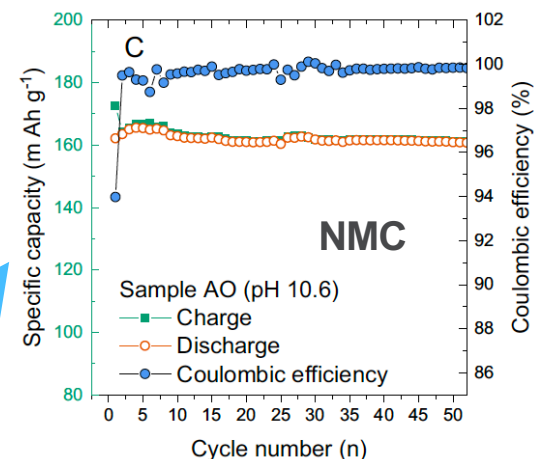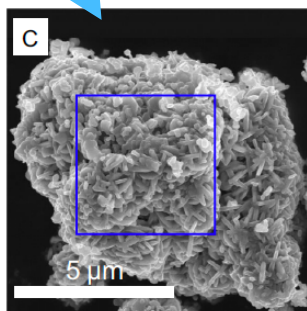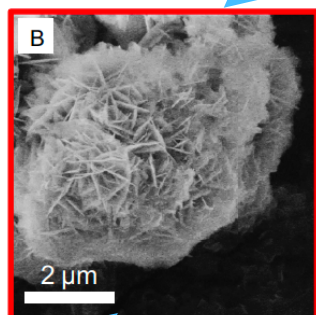- Vincent De Andrade (APS)

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RELEVANCE

NMC cathode, LLZO solid electrolyte

Calcination: lithium source and amount, temperature profile, atmosphere

Coating, drying

Coprecipitation: transition metal salt, buffers, pH, temperature

NMC cathode

LLZO solid electrolyte

Sintering w or w/o pressure, atmosphere

BAT315

LLZO pellet

3

MILESTONES

Serial no.	Milestone description	Completion date	Status
1	Initialize ANL-BNL collaboration on understanding every step of the synthesis, from co-precipitation to sintering, comparing 333 and 811, using *in situ* experimentation and multiscale simulations.	31st December, 2019	Completed
2	Evaluate changes in phase and primary particle size during calcination of NMC 811 by high-resolution powder diffraction in collaboration with BNL. Also evaluate the evolution of microstructure morphology during the sintering of LLZO solid electrolytes.	31st March, 2020	Completed
3	Determine the influence of pH and temperature on facet dependent growth of primary particles from atomistic calculations. Also, incorporate these information into the macroscopic simulations and understand the difference in aggregation of primary particles for various precursor materials.	30th June, 2020	In progress
4	Estimate the effect of dopant segregation during sintering on Li ion conductivity of LLZO solid electrolytes, and predict its impact on overall densification and effective conductivity of LLZO pellets.	30th September, 2020	In progress

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APPROACH: PREDICTING SYNTHESIS ACROSS SCALES AIDED BY *IN SITU* EXPERIMENTATION

Evolution of size, shape, porosity: micro-CT

Secondary particle morphology /density

Microstrcuture macro-homogeneous models
1µm – 1mm

Densification

Particle morphology

Monte Carlo models
Phase field models 10µm – 1mm

Growth/sintering: nano-CT (TXM)

Particle structure & shape

Calcination and sintering

Transport properties

Phase Field Models
Particle Growth Models
100nm – 1µm

Surface energy

Nucleation: SAXS/WAXS

Density Functional Theory
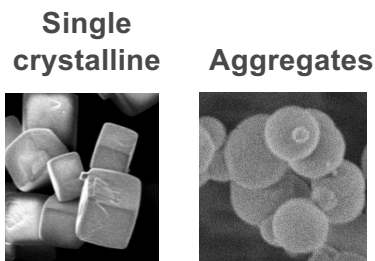Ab-Initio Molecular Dynamics
1Å – 1nm

Co-precipitation (Batch, CSTR)

COPRECIPITATION OF NMC CATHODE PRECURSORS

COPRECIPITATION OF NMC CATHODE PRECURSORS

Different type of particles may form within reactors

Single crystalline   **Aggregates**

Schematic view of a reactor used in coprecipitation process.

Parameters that control particle formation

Rate of reactant addition

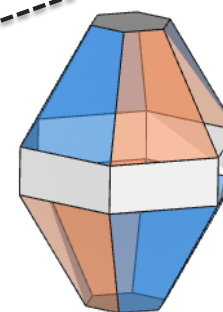**Solubility of the precipitate within solvent**

Rate of reaction

Presence of NH_4OH and air/N_2

Transition metal concentration

Stirrer

Pump

2M MSO_4

Pump

5M NH_4OH

pH meter

Pump

5M Na_2CO_3

60^0C H_2O

1.0M NH_3
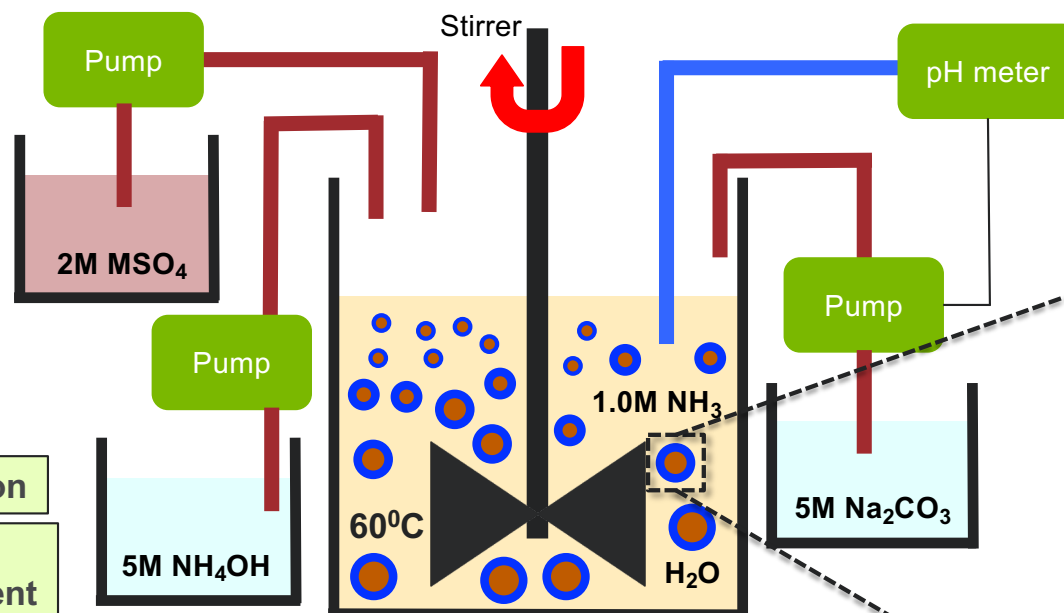
Atomistic view: Each primary particle demonstrates a faceted structure

Different facets have different surface energies and the equilibrium Wulff shape is dictated by the minimum energy surface

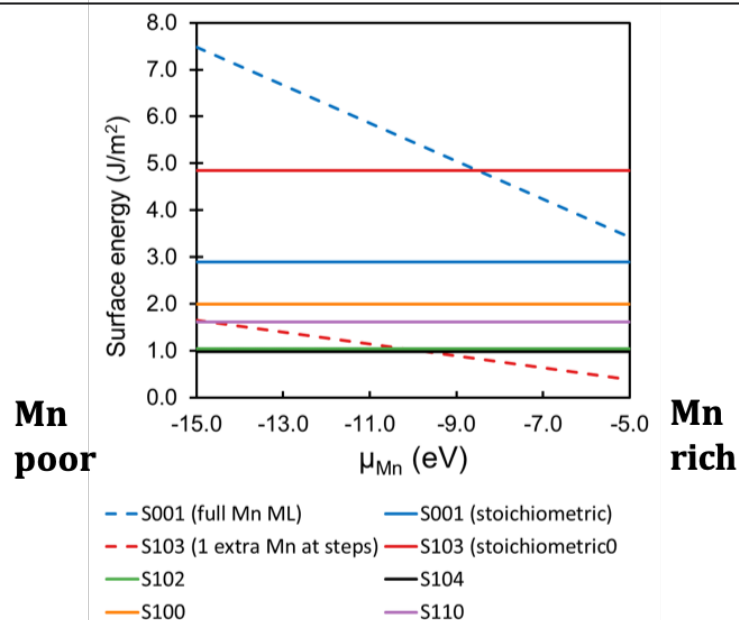**Aggregation ⇔ Surface energy**

Processes during coprecipitation:
1. **Nucleation** of particles
2. **Growth** of particles (usually primary particles)
3. **Aggregation** of particles (secondary particles)

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START WITH ONE TRANSITION METAL: MNCO3
SURFACE ENERGY AND WULFF SHAPE BY DFT

Surface energies of various $MnCO_3$ facets

Mn poor ... **Mn rich**

- - - - S001 (full Mn ML) — S001 (stoichiometric)
- - - - S103 (1 extra Mn at steps) — S103 (stoichiometric0
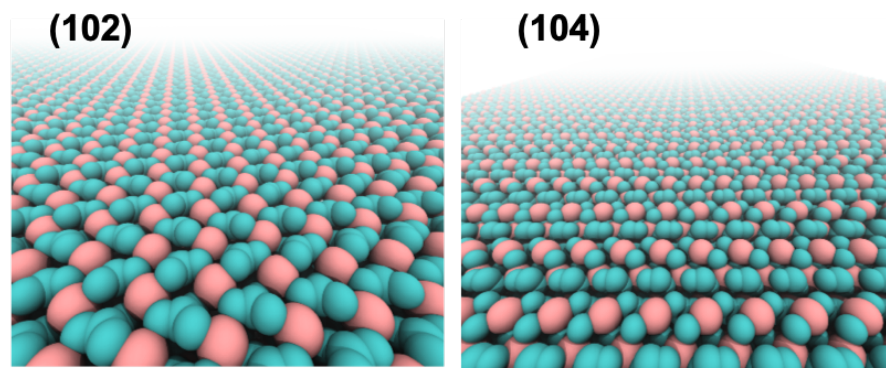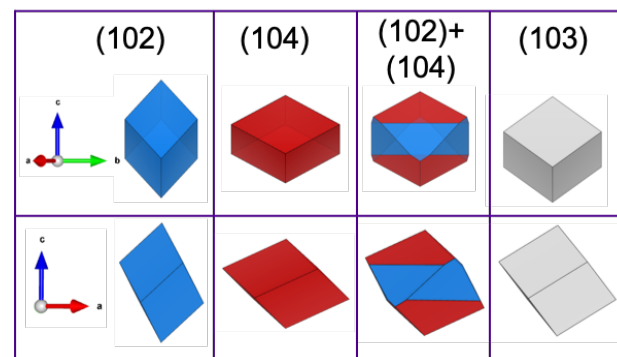—— S102 —— S104
—— S100 —— S110

The lowest energy surface varies according to the chemical potential of Mn within solution.

DFT to Mesoscale:
- Equilibrium Wulff shape of primary particles
- Surface energy densities
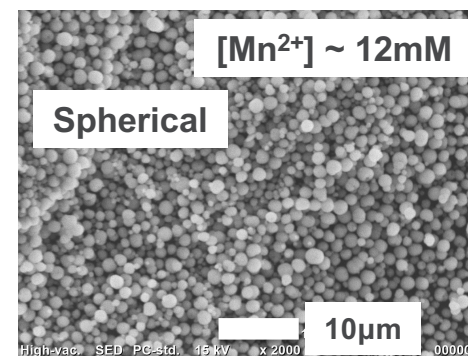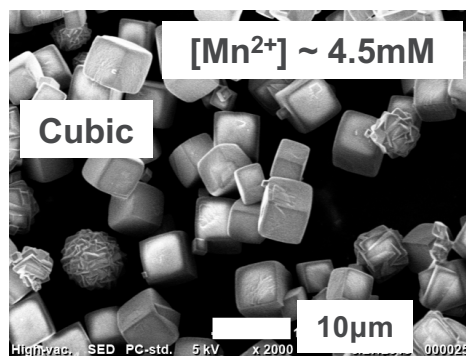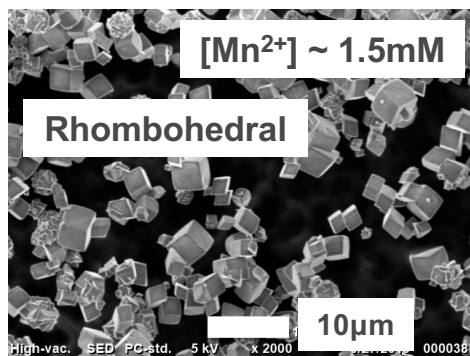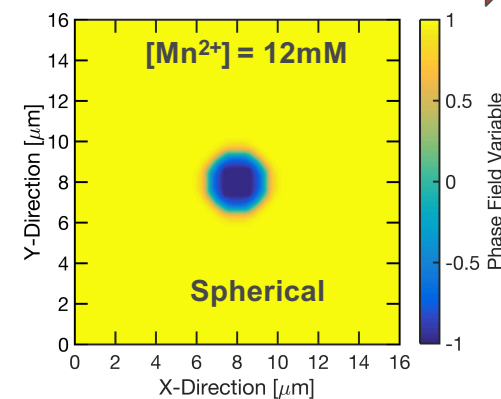
Wulff shape of different low energy $MnCO_3$ facets

(102) | (104) | (102)+(104) | (103)

(102) | (104)

(102) and (104) facets of $MnCO_3$ are most stable

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METAL CONCENTRATION IMPACTS SHAPE

Thermodynamics Dominates
(Rhombohedral Particles)

Kinetics Dominates
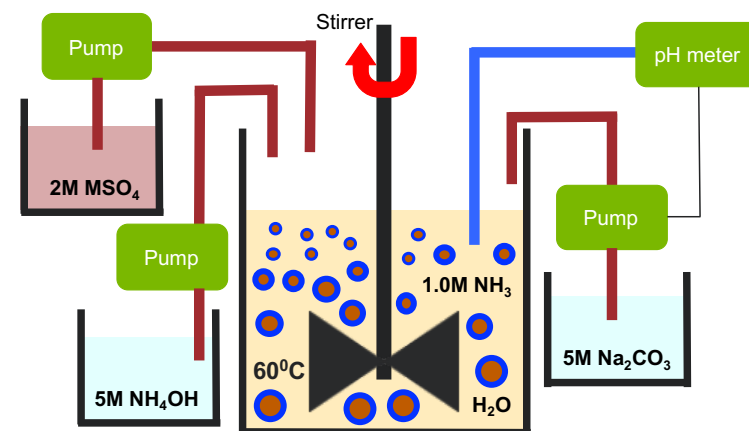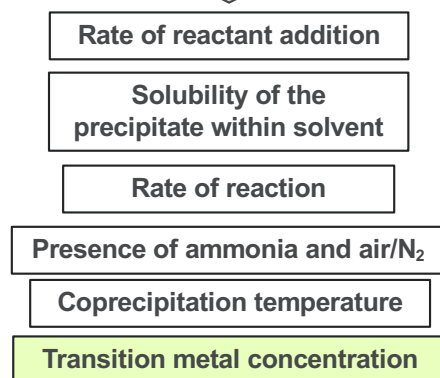**(Spherical Particles)**
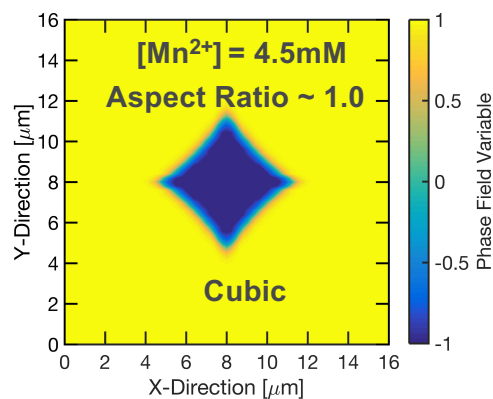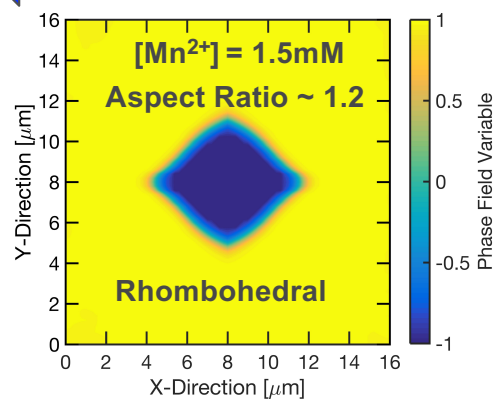
Change in particle shape with Mn^{2+} concentration is consistent with model predictions.
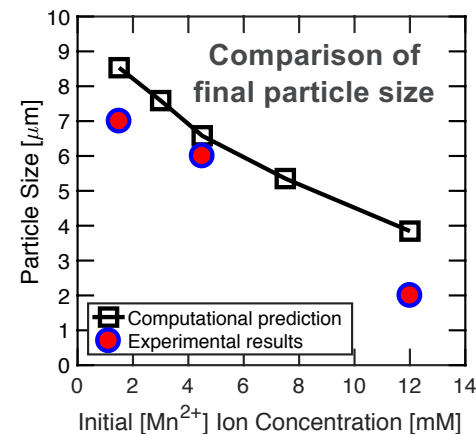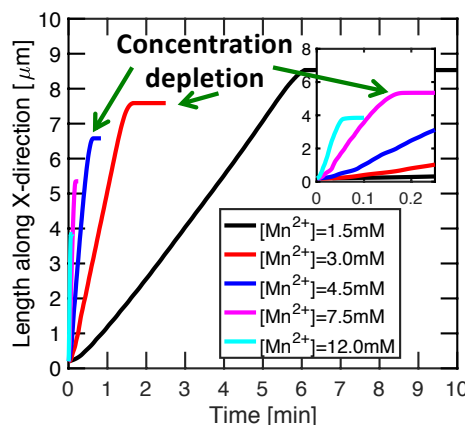
FROM ATOMISTIC- TO REACTOR-LEVEL PROCESSES

As we go to higher length scales (mesoscale), size of individual particles and their growth rates are visualized

Parameters that control particle formation

- Rate of reactant addition
- Solubility of the precipitate within solvent
- Rate of reaction
- Presence of ammonia and air/N_2
- Coprecipitation temperature
- Transition metal concentration

Stirrer
Pump
2M MSO_4
Pump
5M NH_4OH
60^0C
1.0M NH_3
H_2O
pH meter
Pump
5M Na_2CO_3

Phase-field-model-based prediction of particle size evolution with time

- Depletion of reactants causes saturation in particle size
- Final particle size decreases with increasing Mn^{2+} concentration.

Concentration depletion

Length along X-direction [μm] vs Time [min]

[Mn^{2+}]=1.5mM
[Mn^{2+}]=3.0mM
[Mn^{2+}]=4.5mM
[Mn^{2+}]=7.5mM
[Mn^{2+}]=12.0mM

Comparison of final particle size

Particle Size [μm] vs Initial [Mn^{2+}] Ion Concentration [mM]

Computational prediction
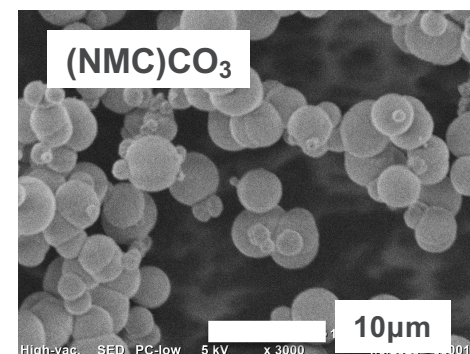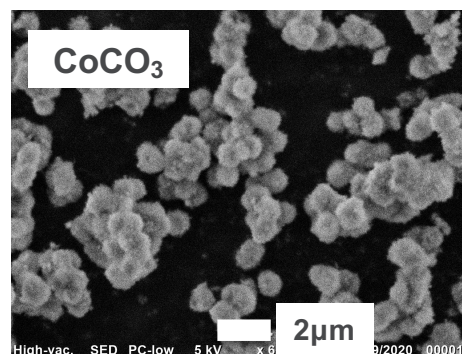Experimental results
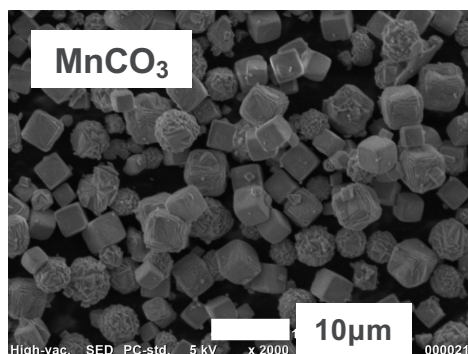
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PRECIPITATION OF Ni, Mn, Co END MEMBERS AND THEIR IMPACT ON NMC PRECIPITATES

Reactor: **Batch**

TM concentration: **4.5 mM**

Time: **30 mins**

- Interestingly, no $NiCO_3$ precipitates were observed after 30 minutes of precipitation

Analysis of precipitation of the end members

- $NiCO_3$ precipitates are not observed due to higher solubility product.
- Simultaneous precipitation of Ni, Mn and Co leads to formation of particle aggregates.

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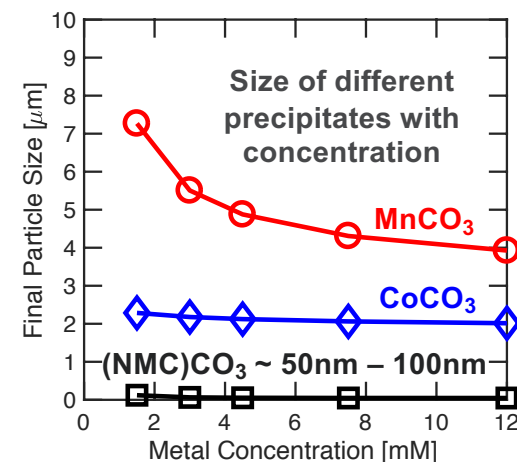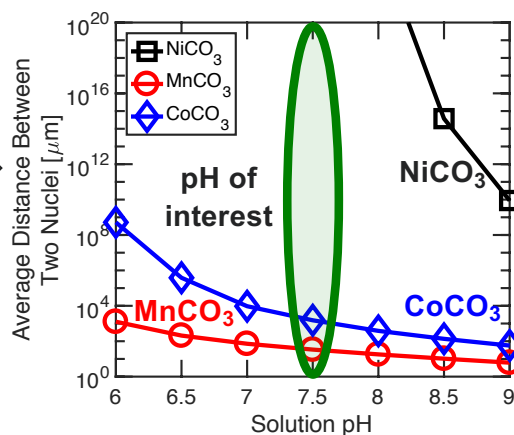
CALCINATION OF NMC PRECURSORS TO CATHODE

CALCINATION INTERMEDIATES

## What phases exists between the melting points of NMC and Li precursors?

- T_{melt} Ni(OH)$_2$ = 235^{0}C
- T_{melt} NiCO$_3$ = 205^{0}C
- T_{melt} Li(OH)$_2$ = 462^{0}C
- T_{melt} Li$_2$CO$_3$ = 720^{0}C

Big gap between melting points of Li and transition metal precursors, especially for carbonates

Big question: What exists between the melting point of the transition metal precursor and the volatilization of the lithium precursor? By XRD we find multiple reaction steps:
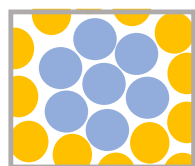
1. Start:
M(OH)$_2$ + LiOH
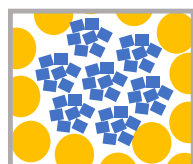
2. T > $T_{melt, TM(OH)2}$
M(OH)$_2$ → MO (811)
M(OH)$_2$ → M$_3$O$_4$ (111)
(nanophased primary particles, but secondary morphology is preserved)
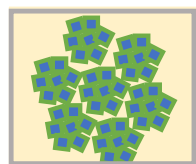
3. T > $T_{melt, LiOH}$
LiOH melts. Initially forms lithium-substituted rock salt phase: Li$_x$M$_{1-x}$O

4. Final layered LiMO$_2$ phase forms at higher lithium stoichiometry

Is lithiating a rock salt phase kinetically favorable?
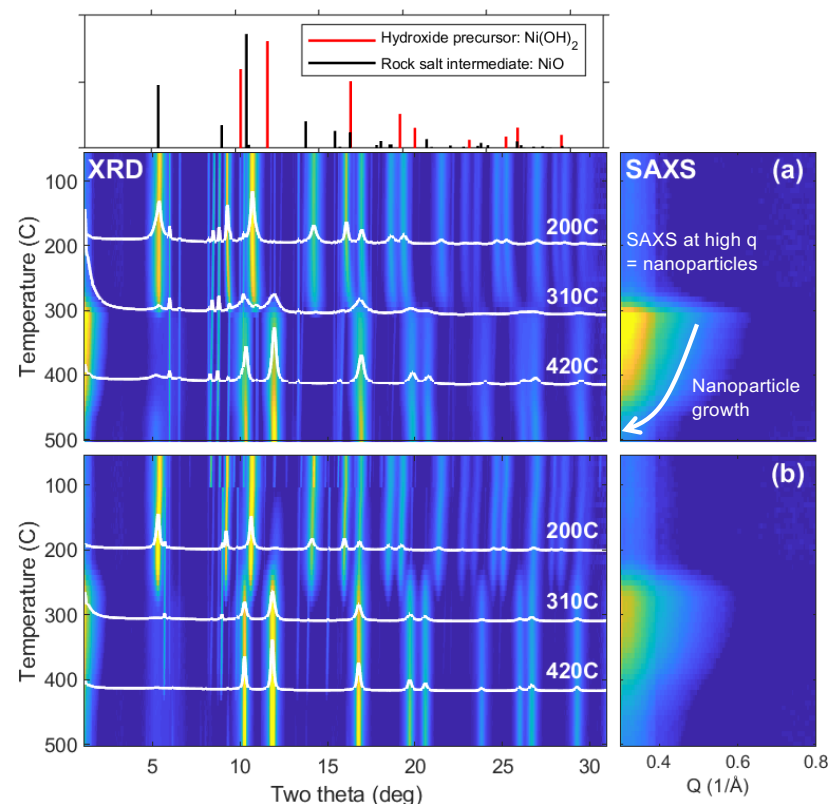
Example: Early temperature behavior of NMC811 precursors mixed with Li2CO3 and LiOH·H$_2$O.
The conversion of hydroxide 811 precursors combined with (a) LiOH·H$_2$O and (b) Li$_2$CO$_3$. Note the peak broadening and the small angle scattering (SAXS) during conversion, indicating the formation of nanoscale rock salt products.

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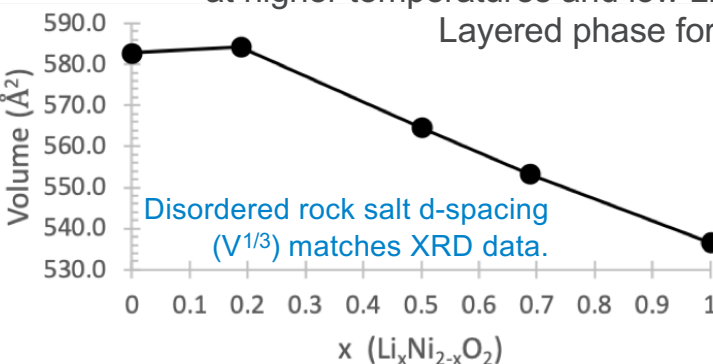# HOW IS LITHIUM INCORPORATED INTO A ROCK SALT LATTICE?

NiO as an exemplar

Interfacial structure: Ab-Initio Molecular Dynamic simulation performed at 1200K for ~100ps.

- Oxygen initially absorbed at the NiO surface to enforce stoichiometry.
- Water formation is clearly seen.
- Ni vacancies are formed at the surface.
- Vacancies are readily filled by Li forming a disordered $LiNiO_2$ layer.
- More $LiNiO_2$ layers start forming.

$$NiO + \frac{1}{4}O_2 + LiOH \rightarrow LiNO_2 + \frac{1}{2}H_2O$$

Lithiated layer

New (Li,Ni)O layer

Ni forms vacancies at the surface

- ○ rock-salt
- ○ Layered
- ● rocksalt (min energy)
- — Rock-salt (convex hull)
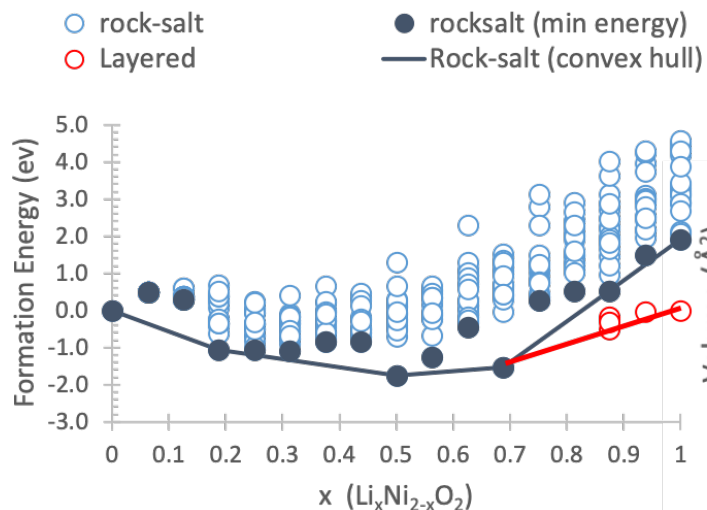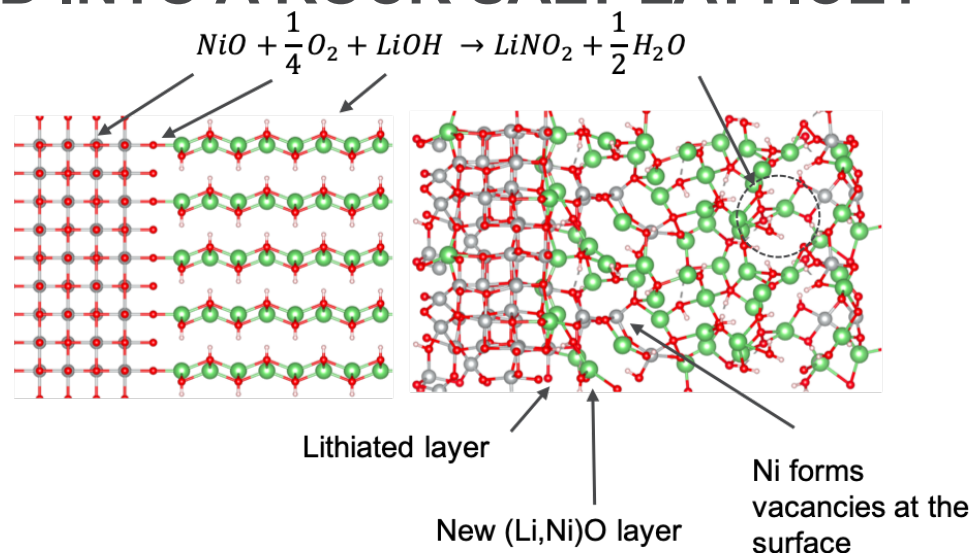
Bulk structure: Disordered rock salt phase is stable at higher temperatures and low Li compositions. Layered phase forms for x > 0.7.

Disordered rock salt d-spacing ($V^{1/3}$) matches XRD data.

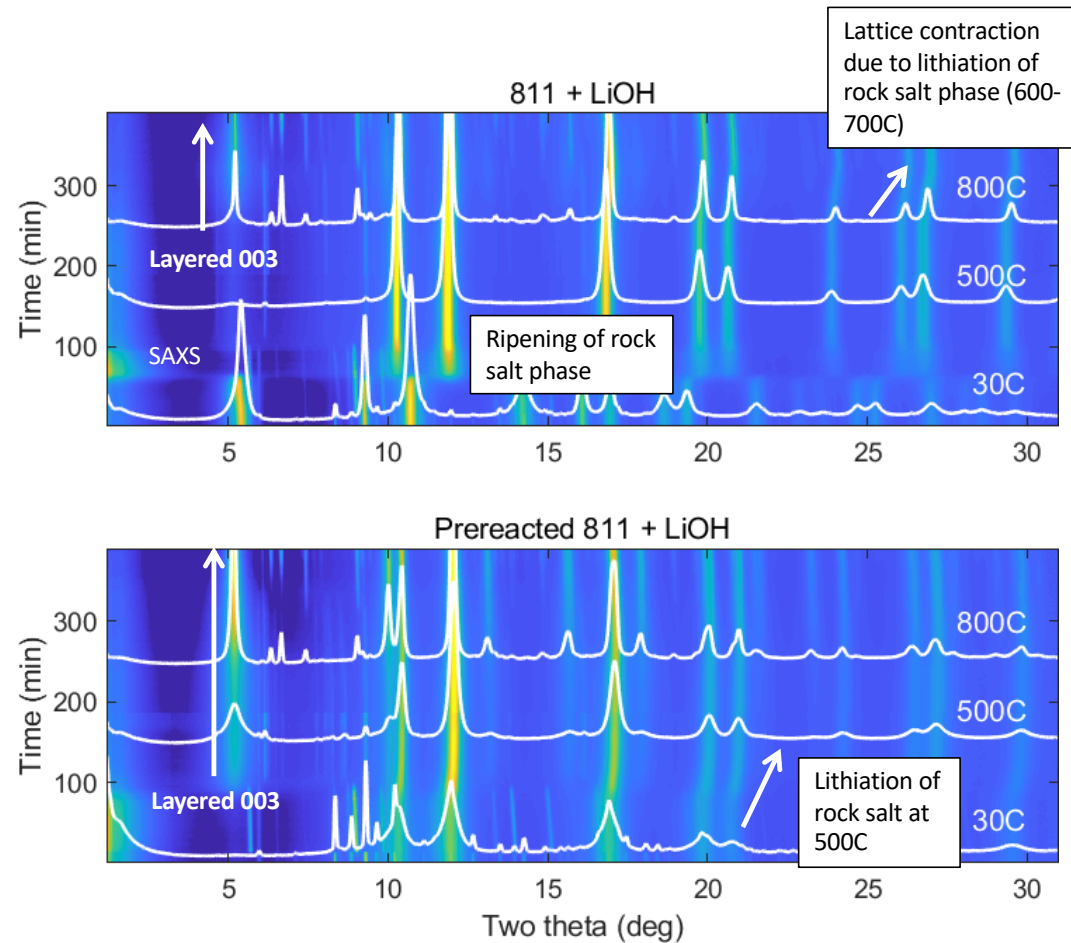**Theory supports formation of rock salt intermediate before conversion to layered**

Formation Energy (ev) — x ($Li_xNi_{2-x}O_2$)

Volume (Å^2) — x ($Li_xNi_{2-x}O_2$)

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HOW CAN WE SPEED UP THE CONVERSION OF ROCK SALT TO LAYERED?

- In air: conversion of LiOH to Li_2CO_3 slows reaction.
- In O_2: Lithiation of the rock salt phase is ultimately the kinetic bottleneck.
- To reduce the size of the rock salt intermediate, we quenched the 811 just after forming the rock salt phase (350C for 4 hours). This pre-reacted 811 precursor has a nanoscale morphology (SAXS, broad XRD peaks).
- The pre-reacted 811 forms the layered phase immediately after LiOH melts, at 500C.

All hydroxide mix: NiO intermediate ripens before LiOH melts, slowing its lithiation

SLOW

FAST
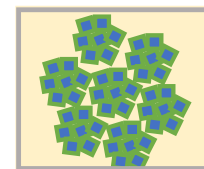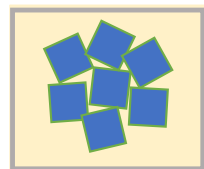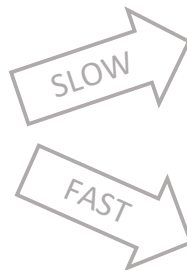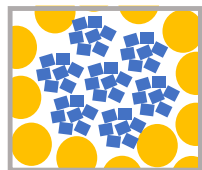
Pre-reacted NMC811 maintains nanoscale primary particles and lithiates immediately when LiOH melts

811 + LiOH

Lattice contraction due to lithiation of rock salt phase (600-700C)

Layered 003

SAXS

Ripening of rock salt phase

Prereacted 811 + LiOH

Layered 003

Lithiation of rock salt at 500C

Two theta (deg)

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PARTICLE RIPENING

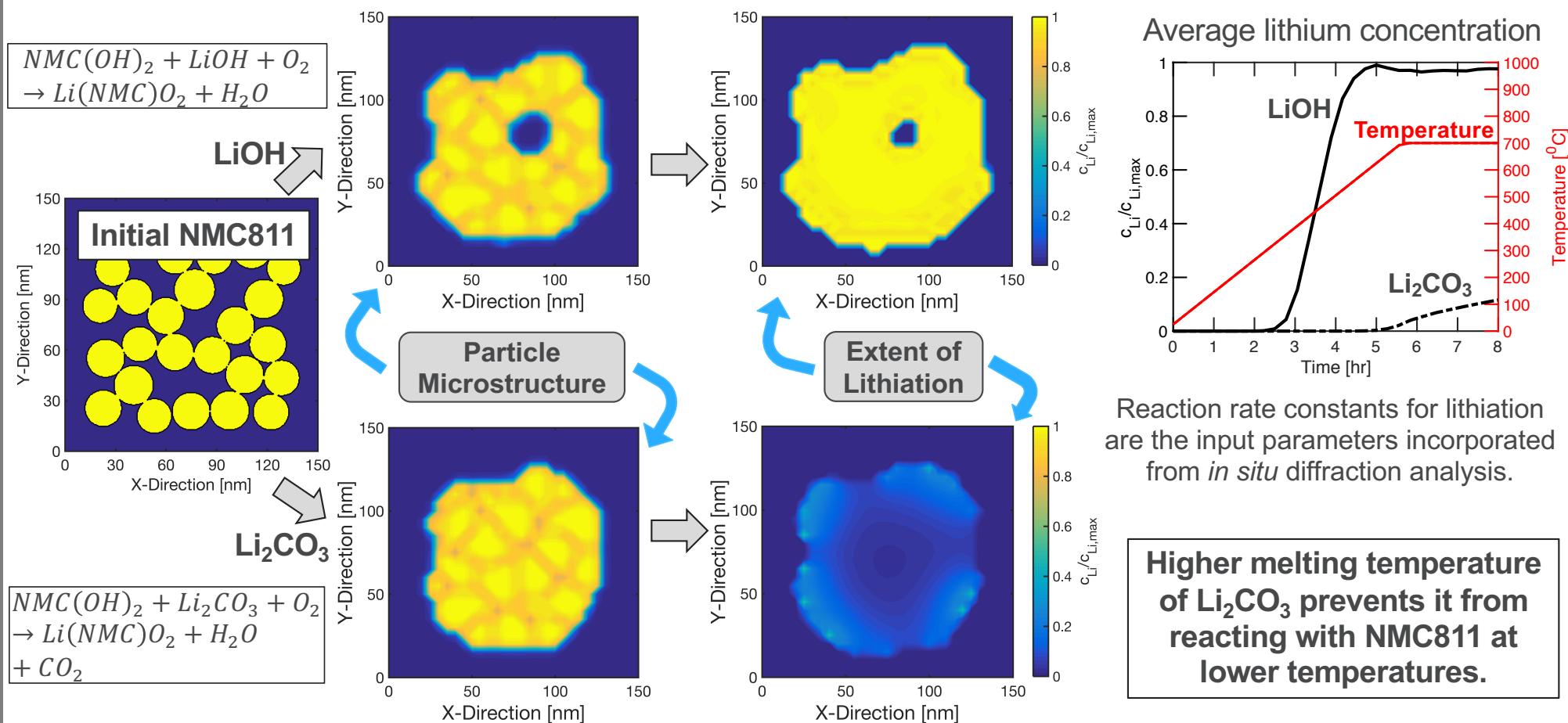**After LiOH melts: a race between rock salt and layered particle growth**

The **amount** of layered phase can be estimated from integrated intensity of 003 peak. The **size** of layered crystallites (i.e. primary particles) can be measured form its full width using the Scherrer equation.

- Pre-reacted NMC (nanophased):
  - Layered phase appears at 500C
  - At 500C: primary particles are only 10 nm
- All-hydroxide mix:
  - Rock salt phase rapidly sinters to ~40 nm crystallites (not shown).
  - This slows their lithiation and conversion to the layered phase. At higher temperature, the primary particles also ripen more rapidly.
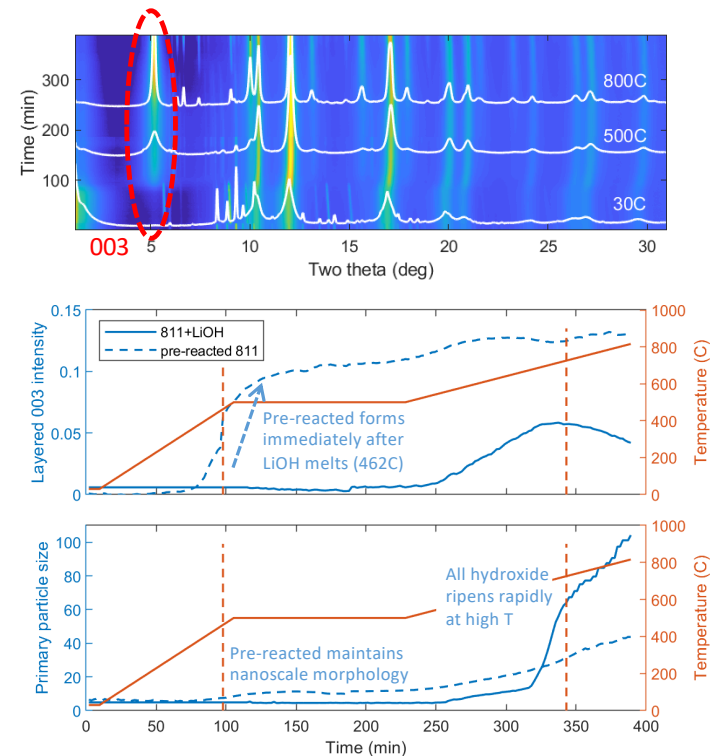
Speed of layered phase formation dictated by a complex interplay between rock salt formation, lithiation, and particle ripening

MODELING THE REACTION-RIPENING DYNAMICS: HYDROXIDE VS CARBONATE

$$NMC(OH)_2 + LiOH + O_2 \rightarrow Li(NMC)O_2 + H_2O$$

LiOH

Initial NMC811

Li$_2$CO$_3$

$$NMC(OH)_2 + Li_2CO_3 + O_2 \rightarrow Li(NMC)O_2 + H_2O + CO_2$$

Particle Microstructure

Extent of Lithiation

Average lithium concentration

LiOH

Temperature

Li$_2$CO$_3$

Reaction rate constants for lithiation are the input parameters incorporated from *in situ* diffraction analysis.

Higher melting temperature of Li$_2$CO$_3$ prevents it from reacting with NMC811 at lower temperatures.

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CALCINATION OF LZO TO LLZO AND ITS DENSIFICATION

LLZO SOLID STATE ELECTROLYTE: DENSIFICATION AND GRAIN STRUCTURE

Synthesis of LLZO particles involve two steps	→	1. Conversion of LZO to cubic LLZO in the presence of Li-source	+	2. Densification of synthesized LLZO and formation of dense pellets

Aim: Formation of cubic-LLZO particles with high ionic conductivity

Aim: Prepare very dense pellets by applying high pressure and temperature

SEM image of LLZO

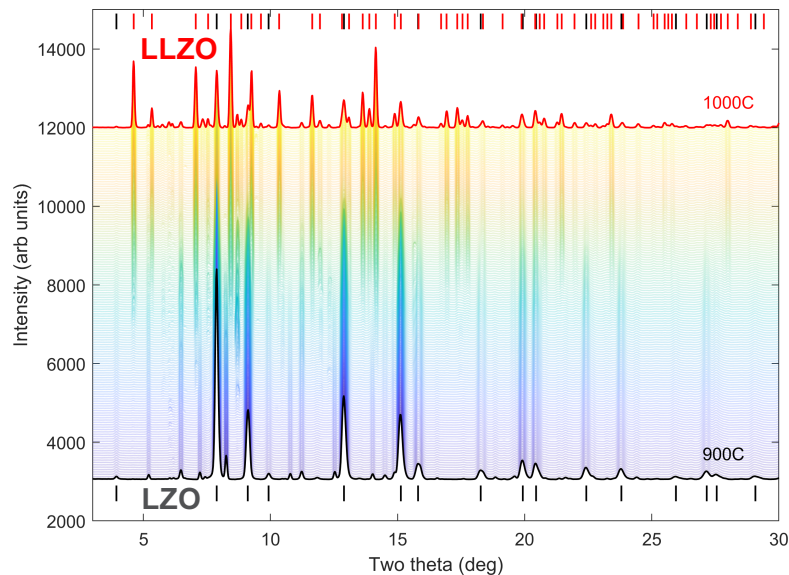Sintered LLZO particles

3μm

Void space
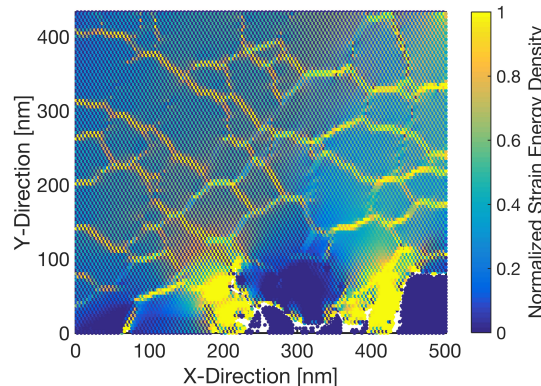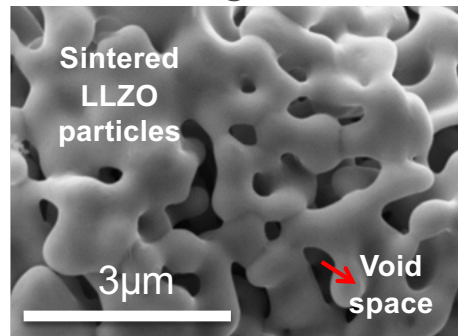
Current focusing and propensity of fracture initiation at the grain-boundary region
(Source: Srinivasan et al., Project ID: BAT309)

Investigate the synthesis of LLZO in order to maximize conductivity and minimize current focusing at the grain-boundaries.

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TRACKING LZO CONVERSION TO LLZO *IN SITU*

Calcination of green powder (obtained from MERF, ANL) conducted at APS to understand the formation of cubic LLZO phase and grain ripening. (Temperature ramp rate: **10^0C/min**)

LZO + Li_2CO_3 → LLZO

Particle Size Evolution: Experiments

LLZO ($2\theta = 14.1$)
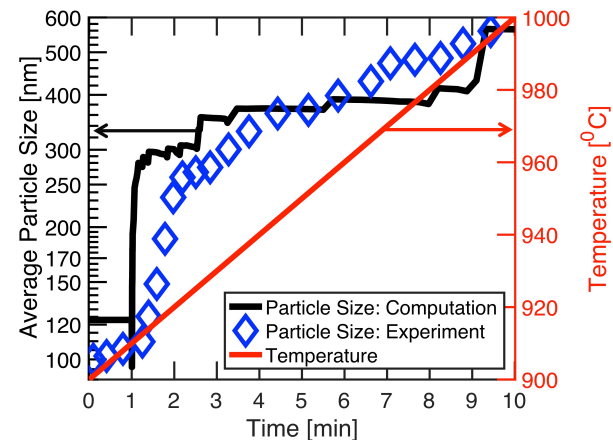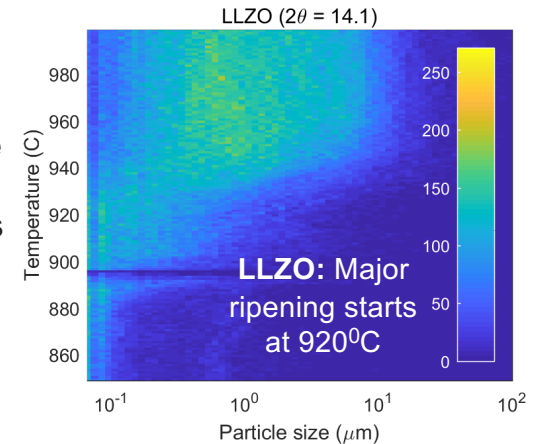
LLZO: Major ripening starts at 920^0C

Conversion from LZO to LLZO starts at around 900^0C to 920^0C.

Input for computational model:
- Initial size of LLZO is assumed to be 100nm.
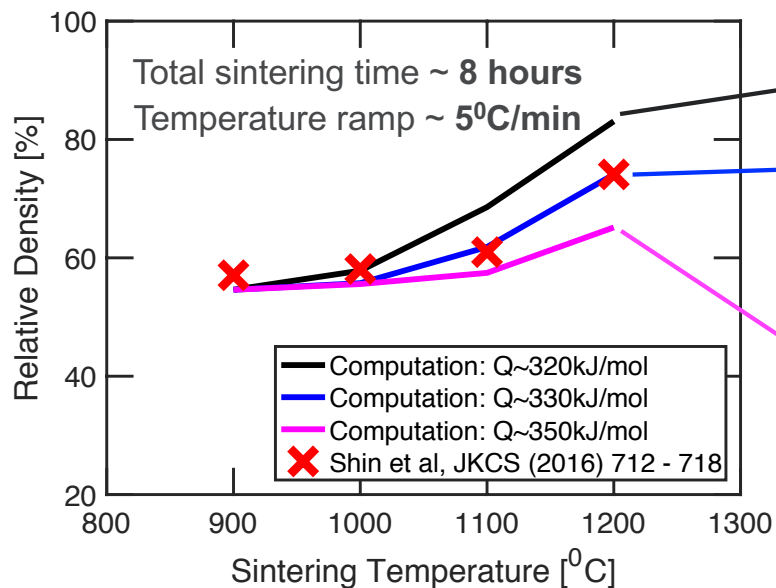

Good correlation with experiments necessitates, Q ~ 300 kJ/mol.

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FROM CALCINATION TO DENSIFICATION: MODELING THE SINTERING PROCESSS

Simulation of the LLZO densification process using phase field model.

Total sintering time ~ **8 hours**
Temperature ramp ~ **5⁰C/min**

Legend:
- Computation: Q~320kJ/mol
- Computation: Q~330kJ/mol
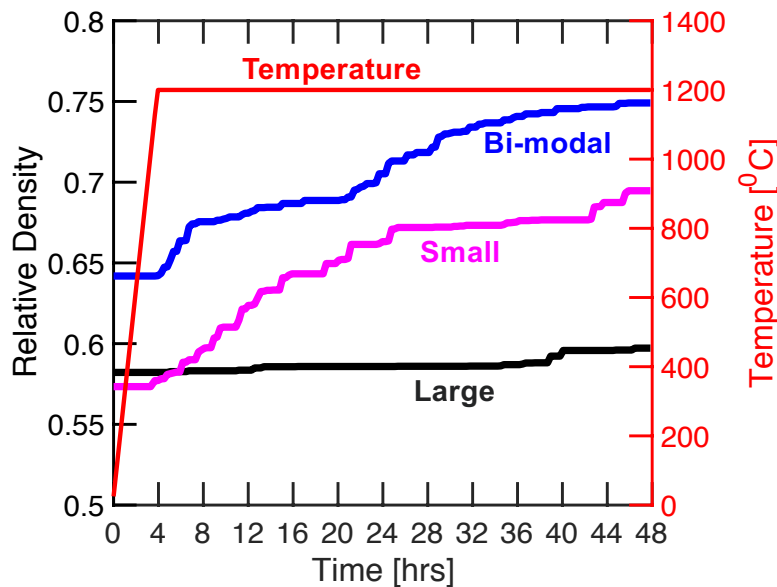- Computation: Q~350kJ/mol
- ✖ Shin et al, JKCS (2016) 712 - 718

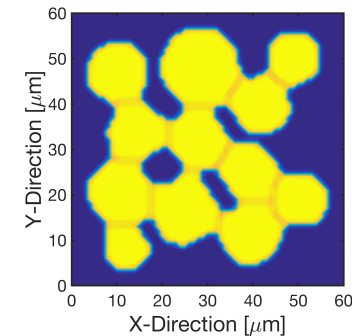An activation energy of 330kJ/mol gives the best fit with experimental results.
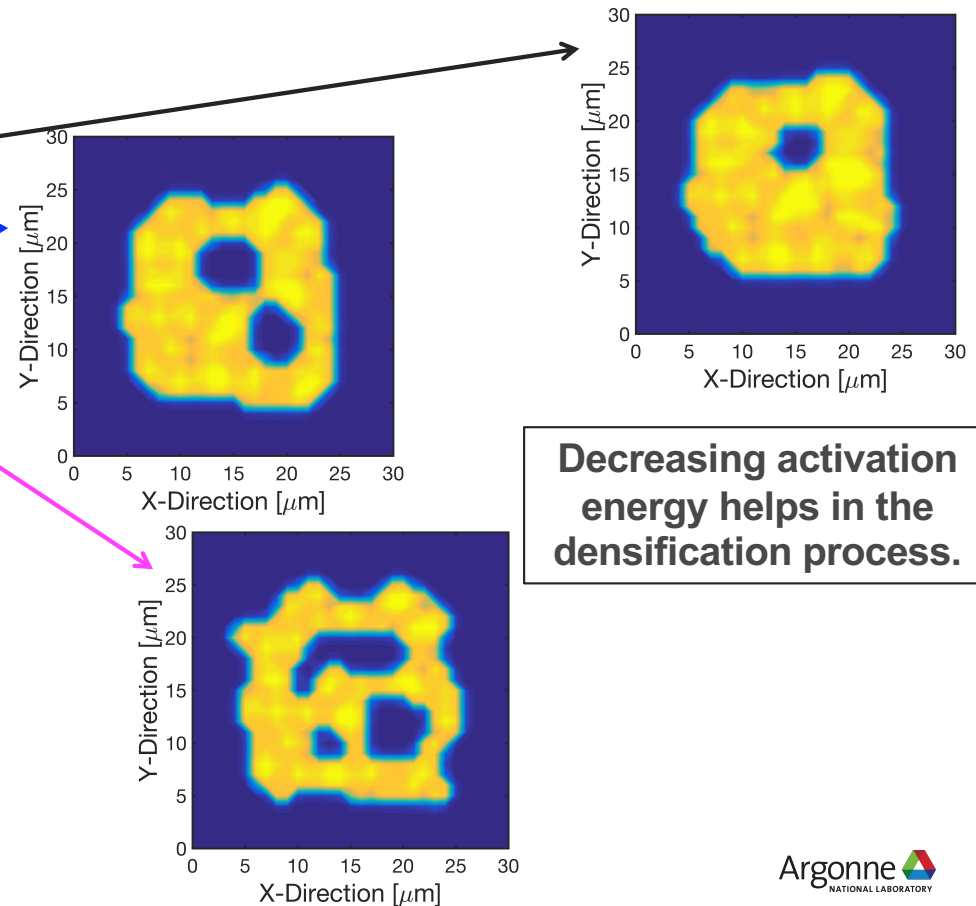
Decreasing activation energy helps in the densification process.

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IMPACT OF SIZE AND SIZE DISTRIBUTION OF LLZO PARTICLES ON THE DENSIFICATION PROCESS

Increase in relative density
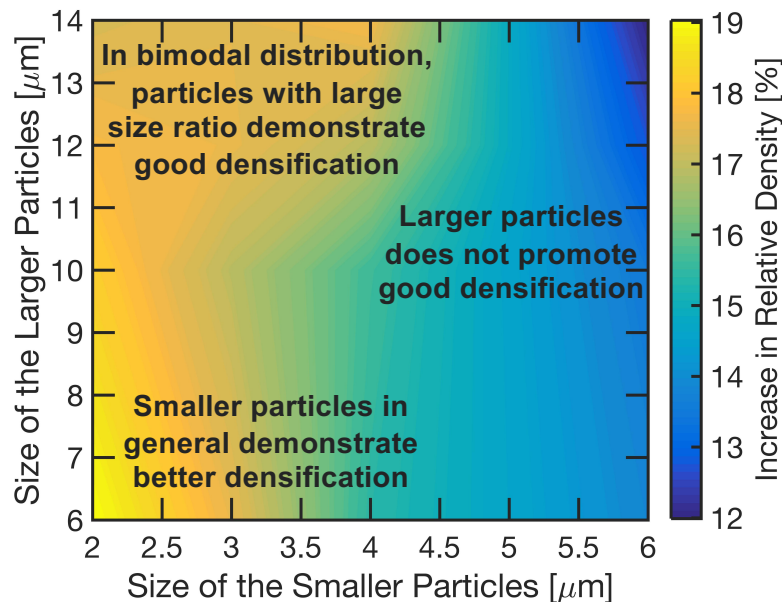
Small	Large	Bi-modal
12.5%	1.5%	10.5%
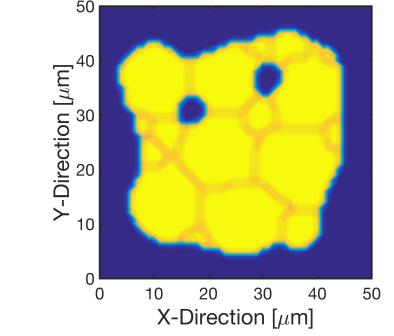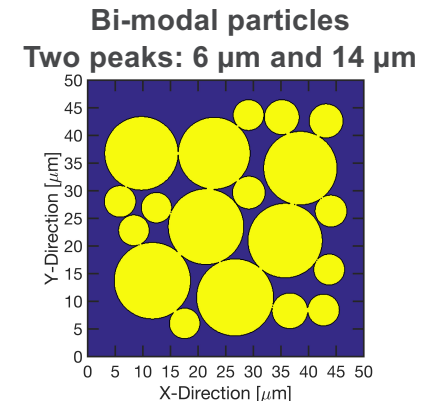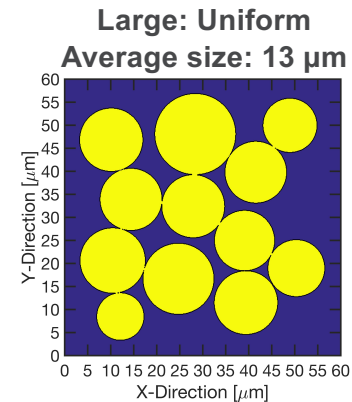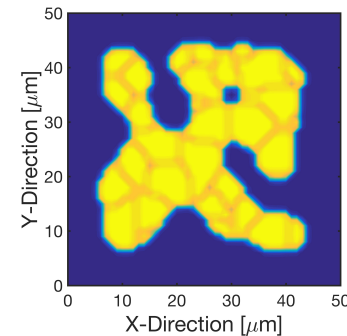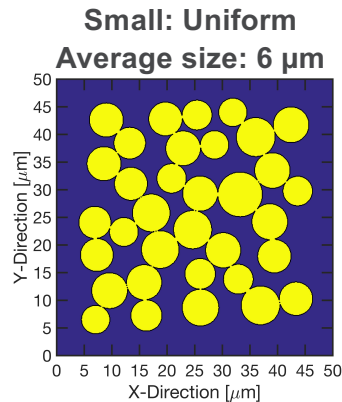
- Microstructures with bi-modal particle size distribution demonstrate higher relative density
- Microstructures with smaller particle size show higher "increase in relative density"

OPTIMUM PARTICLE SIZE AND SIZE RATIO FOR BEST DENSIFICATION OF LLZO
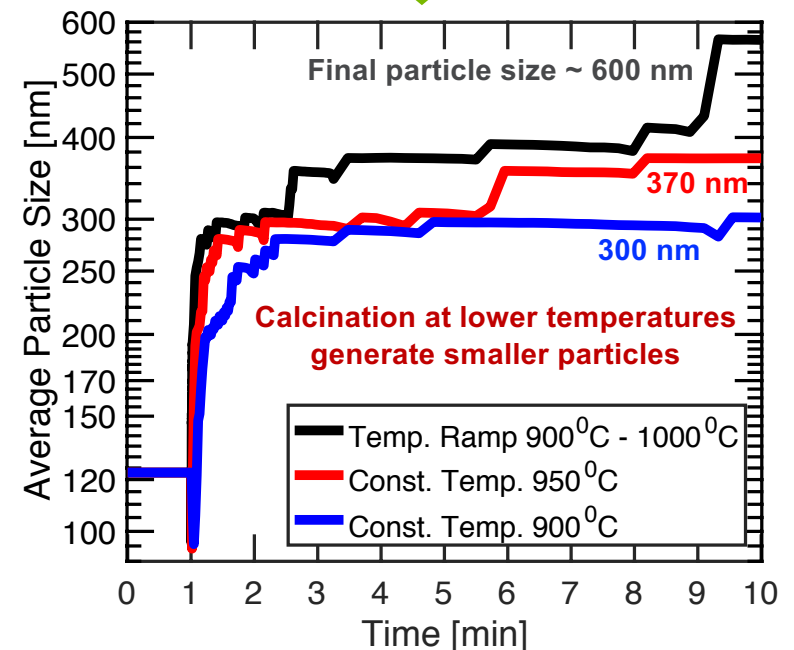
Densification simulations run for 48 hours at 1200^0C

In bimodal distribution, particles with large size ratio demonstrate good densification

Larger particles does not promote good densification

Smaller particles in general demonstrate better densification

Size of the Larger Particles [μm]

Size of the Smaller Particles [μm]

Increase in Relative Density [%]

Bi-modal particle size distribution with smaller particles are beneficial for densification of LLZO.
- **Small sized cubic-LLZO particles can be obtained by calcining at lower temperatures, such as, 900^0C.**

Small sized cubic LLZO particles are beneficial for obtaining better densification

How can we modify the calcination process for generating smaller particles?

Final particle size ~ 600 nm

370 nm

300 nm

Calcination at lower temperatures generate smaller particles

Average Particle Size [nm]

Temp. Ramp 900^0C - 1000^0C
Const. Temp. 950^0C
Const. Temp. 900^0C

Time [min]

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RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

This project was not reviewed last year.

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COLLABORATION AND COORDINATION

- Argonne Natioanl Laboratory (ANL)
  - Gregory Krumdick and Joseph Libera (MERF), Project ID: BAT315
  - Jason Croy and Arturo Gutierrez (CSE), Project ID: BAT049
  - Ozge Kahvecioglu and Shankar Aryal (MERF), Project ID: BAT167
  - Jianguo Wen and Ilke Arslan (CNM)
  - Vincent De Andrade (APS)

- University of Chicago
  - Joanne Stubbs and Peter Eng. (APS, ANL)

- Brookhaven National Laboratory (BNL)
  - Feng Wang and Jianming Bai, Project ID: BAT183

- DOE User Facility
  - Advanced Photon Source (APS), located in ANL
  - Center for Nanophase Materials (CNM), located at ANL
  - Laboratory Computing Resource Center (LCRC), located at ANL

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REMAINING CHALLENGES AND BARRIERS

- The developed DFT based atomistic modeling technique assumes only the reaction with hydrogen and/or oxygen while estimating the equilibrium configuration of precursors. However, in the presence of carbonate and ammonia ions in the solution, the equilibrium picture can be very different, which can significantly impact its surface energy and Wulff shape.

- The phase field based methodology captures the sintering behavior in 2D scenario. However, the real systems operate in a 3D structure.
  - ➤ In order to capture the collective behavior of multiple grains in 3D, a homogenized sintering model may be required.

- Estimation of exact grain-boundary mobility during sintering, or measurement of particle shape evolution during coprecipitation and/or sintering, has not been attempted, but should be addressed for obtaining a good set of experimental data that can inform the computational models regarding the relevant physics.

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FUTURE WORK PLANS

Coprecipitation:
- Understanding why certain synthesis processes lead to single crystals and others give aggregated secondary particles.
- Understanding coprecipitation of cathode particles with composition gradient.

Sun et al., Nat. Mater. (2012) 942
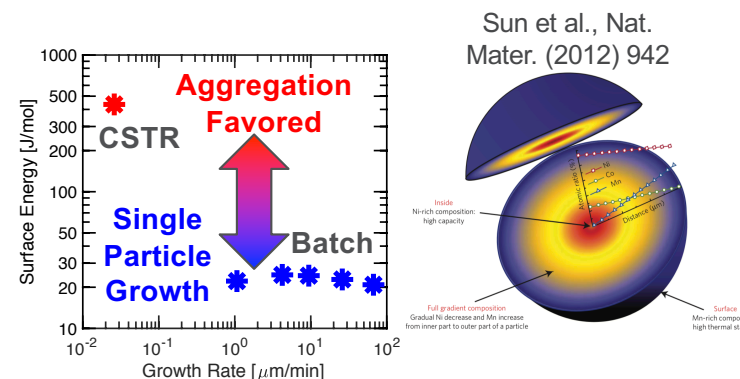
Calcination:
- TXM analysis of particle evolution during calcination.
- Investigation of the applicability of lower melting point lithium sources in lowering the calcination temperature.
- Use model as a guide to develop synthesis pathways that speed cathode formation
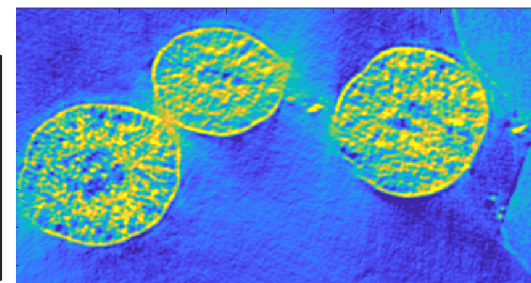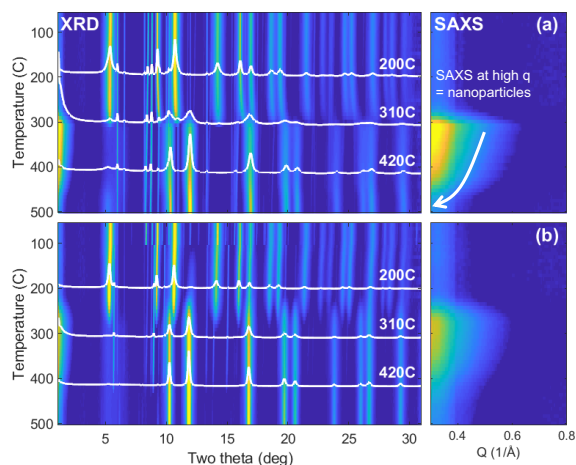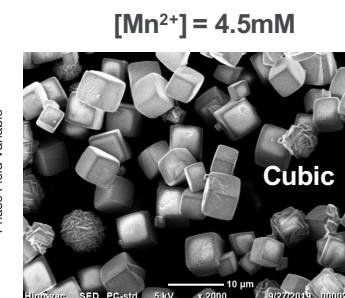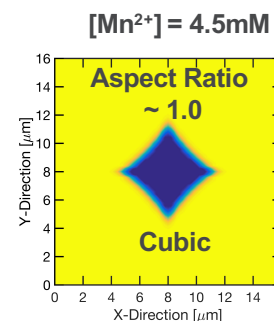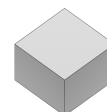

Densification:
- Impact of externally applied pressure on the overall densification of the LLZO pellets.
- Experimental estimation and visualization of the LLZO densification process (at APS ANL).
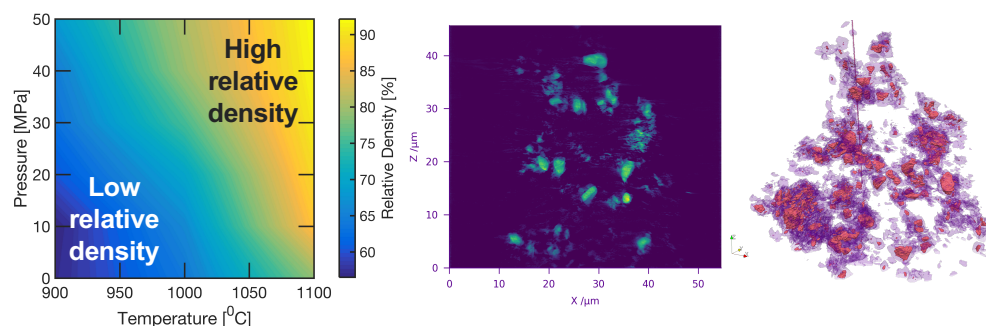
SUMMARY

Coprecipitation: Shape and size of MnCO$_3$ coprecipitates as predicted by DFT and mesoscale calculations correlate well with the experimental observations.

(103)

[Mn^{2+}] = 4.5mM

[Mn^{2+}] = 4.5mM

Calcination: In situ characterization of the calcination of NMC with different lithium sources reveal the differences in lithiation mechanism and the corresponding particle size evolution.

Densification: Analyzing densification of LLZO reveals that bimodal size distribution with smaller particle sizes is beneficial for better densification of the LLZO sample.

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